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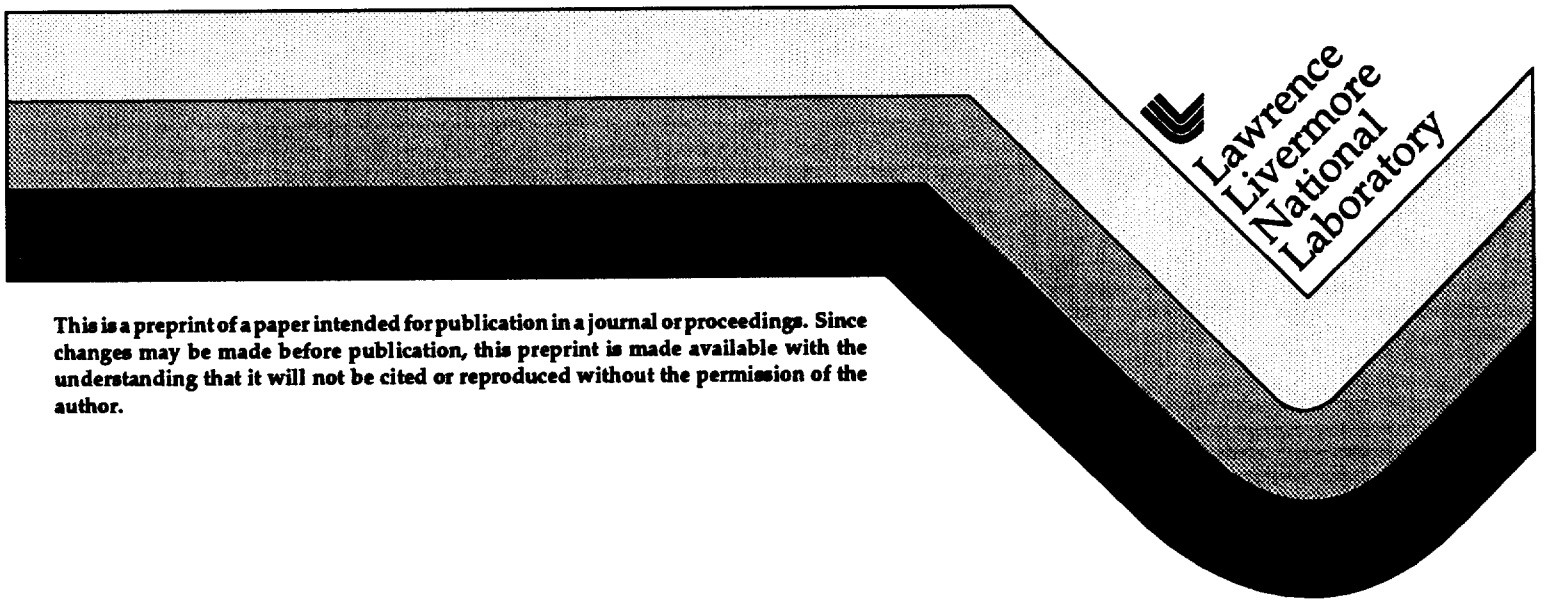

A new class of diode-pumped, mid-IR, broadly-tunable lasers based on TM^{2+} ions in T_d coordination: Cr^{2+}:ZnX (X=S,Se).

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Abstract

A new class of room-temperature, diode-pumped solid state lasers, that are broadly tunable in the mid-infrared spectral region, has been conceptualized and demonstrated. These lasers are based on intra-ion transitions of divalent transition metals placed in substitutional cation sites of tetrahedral symmetry in large bandgap chalcogenide semiconductor crystals. These combinations of laser-ions and host crystals are seen to provide favorable radiative and non-radiative transition processes for the realization of the desired laser performance characteristics. Spectroscopic data for candidate schemes are reviewed and divalent chromium doped zinc chalcogenides are identified as potentially superior laser candidates. Preparation of laser quality Cr^{2+}:ZnSe crystals is described and experimental results to date for a diode-pumped laser are given. Remaining laser development issues are discussed briefly.

Keywords: diode-pumped, tunable, solid state laser, divalent chromium

INTRODUCTION

The invention and development of the titanium doped sapphire (Ti:S) laser gain crystal by Moulton [1] in 1985 launched a new era in laser applications. As is well known, this laser crystal is characterized by a broad pump absorption band peaked near 500 nm, and a broad (~2300 cm^{-1}) Stokes-shifted emission band centered near 800 nm. These bands arise from electronic transitions between the ground $^2T_2$ and excited ^2E levels of the ground d^2 electronic configuration of the Ti^{3+} ion, situated in the distorted octahedral Al^{3+} sites of the Al_2O_3 lattice. The crystal field induced electric dipole transition moment results in a radiative lifetime of ~4 microseconds and peak absorption and emission cross sections of ~3 x 10^{-19} cm^2. These spectroscopic characteristics have enabled the design and practical realization of novel Ti:S solid state lasers with a wide variety of output waveforms: tunable emission [2] from ~680-1065 nm; pure CW room temperature operation at the multi-watt power level [3]; gain-switched pulsed operation [4]; mode-locked operation with pulsewidths ~11 fsec [5]; amplification of chirped pulses to the multi-terawatt level [6]. When combined with nonlinear conversion elements (doublers, mixers, optical parametric generators, etc.), the Ti:S laser has become a nearly ubiquitous source of ultra-short-pulse tunable radiation in the ultraviolet, visible, and infrared regions for use in scientific, biological, medical, military, commercial, and industrial applications.

In view of the success of the Ti:S laser, one might well seek analogous laser gain media operating in other spectral regions, vis., the mid-infrared. In contrast to the Ti:S laser, such a laser could in principle also be directly pumped by powerful InGaAsP semiconductor laser diode arrays. This new laser type would be useful in directly generating radiation within the 2000-3000 nm mid-IR transmission window of the atmosphere for use in remote-sensing applications. Figure 1 shows this atmospheric transmission window and summarizes the desired features of a

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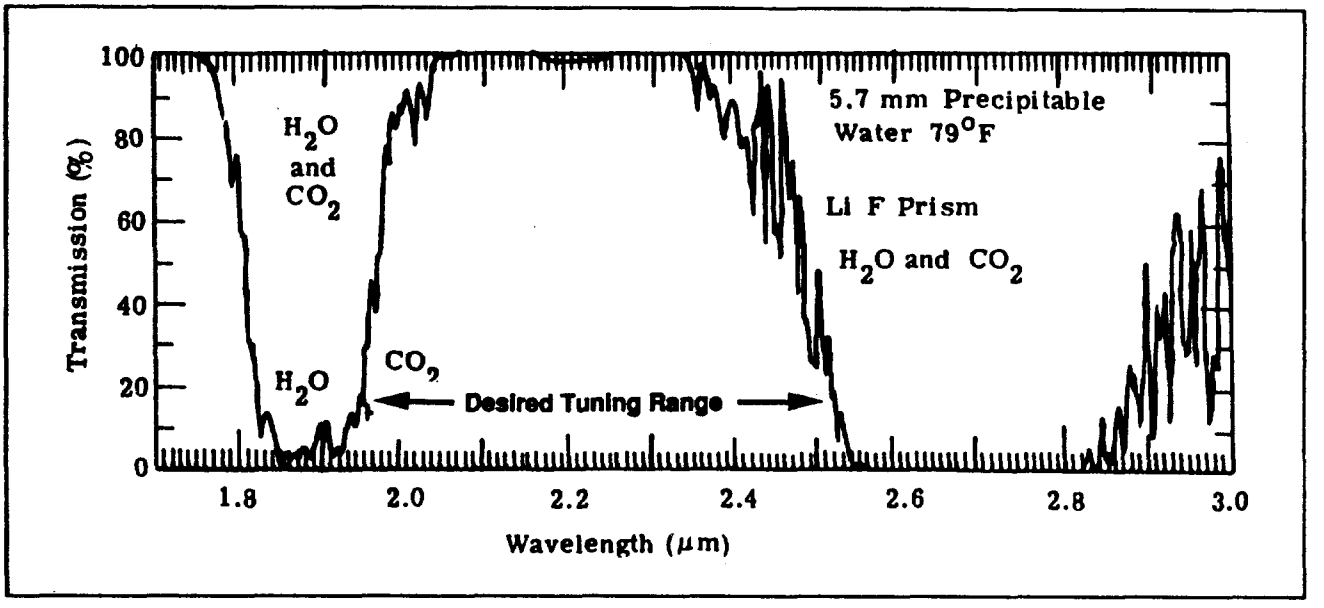

Compact (Diode Pumped)	**Waveform: Q-switched, >50 kHz rep rate**
Output Power, >10 Watts	**Tunable Ranges: 2.0 — 2.6 microns**
Operating Temperature, 300 K	**Efficiency, >5% (air platform)**

Figure 1. Remote-sensing application in the 2-3 micron atmospheric transmission window. Desired characterisitics of a diode-pumped tunable solid state laser source are given.

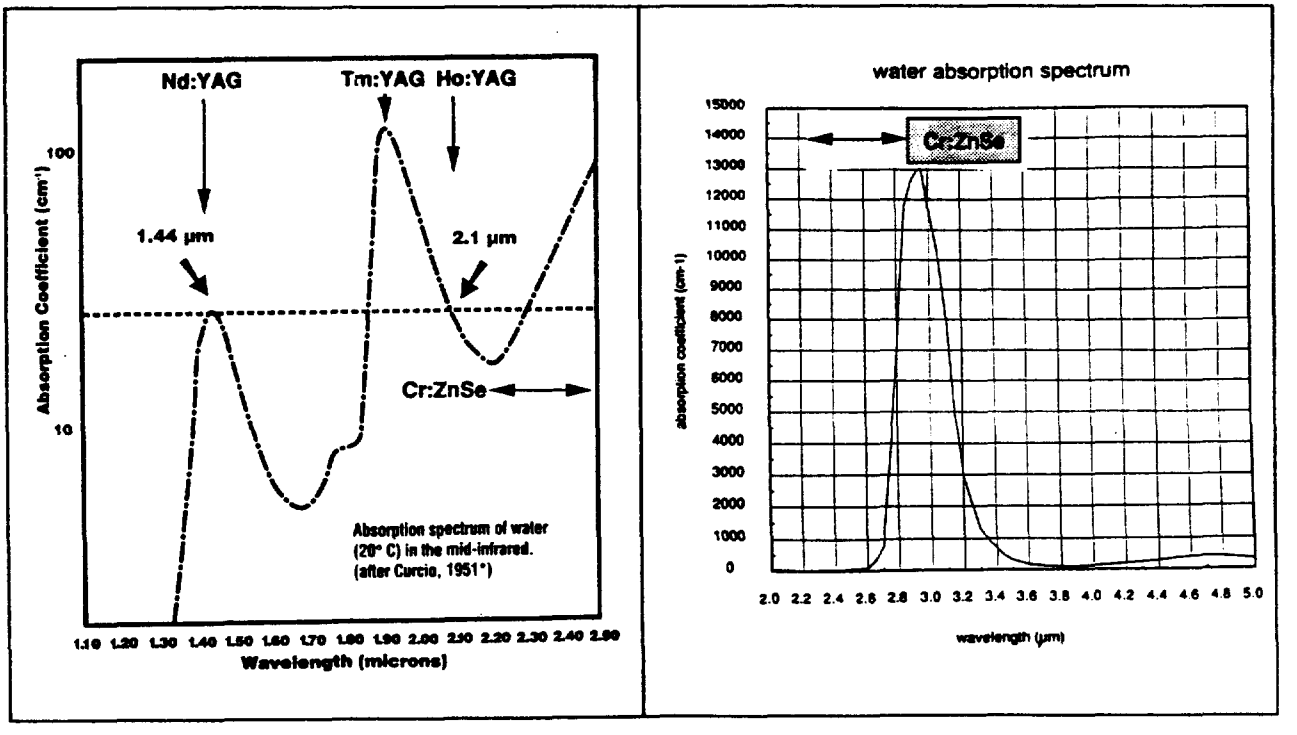

Figure 2. Absorption coefficient of water in the 2-4 micron region. Anticipated tuning range of a Cr^{2+}:ZnSe diode-pumped solid state laser.

tunable diode-pumped solid state laser for remote sensing applications. Such mid-IR lasers might also serve as wavelength tunable sources of high power radiation in the 2000-3000 nm region for therapeutic medical applications. Figure 2 shows the absorption coefficient of water (containing tissue) in this spectral region. By tuning across the short wavelength side of the intense water absorption band peaked at ~2950 nm, a surgeon could continuously adjust the depth of penetration of the applied radiation by over three orders of magnitude (from mm to microns) using a single tunable laser source. Because of its broad spectral gain bandwidth, the laser could also be configured to generate tunable sub-picosecond pulses, permitting a high ablation rate of tissue while incurring very little transfer of thermal energy to the supporting tissue [7]. The main question then is, "What class of laser active ions and crystalline hosts possess the required static and dynamic spectroscopic characteristics needed for an infrared "Ti:S" laser?"

CANDIDATE LASER ION AND CRYSTAL HOST TYPES

The fundamental reason for the lack of a room temperature, broadly tunable, mid-IR solid state laser is the relative paucity of luminescent materials in that spectral region. The usual explanation for this "long wavelength cut-off" of luminescence is the rapid on-set of radiationless decay associated with multi-phonon emission (MPE), [8]. As the electronic transition "energy gap" declines with increasing emission wavelength, the MPE rate overtakes and ultimately overwhelms the radiative transition rate, quenching the luminescence. Thus, we need to identify ion/host systems for which the radiative decay rate is comparatively high and the radiationless decay rate is comparatively low.

As is well known, crystals containing progressively heavier anions also are characterized by smaller (maximum) phonon energies. In such crystals, greater numbers of phonons (and correspondingly high-order multiphonon processes) are required to span a given electronic transition energy gap, and are more likely to manifest long wavelength luminescence.

As potential laser ion candidates for the desired class of mid-IR lasers, transition metal ions offer many desirable characteristics. Their free-ion ground electronic configurations are formed by d-electrons which interact rather strongly with lattice anions, often giving rise to absorption/emission spectroscopic features characterized by large Stokes shifts (thousands of wavenumbers). The band emission characteristics resulting from such Stokes shifts offer the potential for obtaining broadband optical gain and the generation of ultra short pulses.

When a transition metal ion is substitutionally incorporated into a crystalline host, electric dipole transitions are induced between its d^n electronic levels, as a result of odd-parity crystal field components produced at the cation substitutional site by lattice anions. Since we desire the laser transition to have a relatively high radiative transition rate (so as to dominate any radiationless decay mechanisms), we should consider crystals with heavy anions and substitutional cation sites with high asymmetries (e.g. T_d symmetry). Perhaps the simplest physical system meeting these general criteria is the following: TM^{2+}:MX, where M = Zn, Cd and X = S, Se, Te, and where TM^{2+} = divalent transition metal ion.

As a class, divalent transition metal doped II-VI crystals possess several important features. First is the existence of many chemically-stable divalent transition metal ions which readily substitute for the M=Zn, Cd divalent cations of MX crystals (with no need for charge compensation and little disturbance of the host crystal lattice). An additional feature of II-VI crystals is their tendency to crystallize in the wurtzite and sphalerite structures whose cation sites are tetrahedrally coordinated. This provides the strong odd-parity crystal field components at the cation site needed for significant mixing of opposite parity metal ion p-electronic wavefunction into the ground d^n configuration. The low phonon energies of these heavy cation hosts give rise

to high IR transparency and reduced multi-phonon decay rates. Mid-IR luminescence of several TM^{2+} ions in ZnX crystals have been extensively reported in the literature [9]. DeLoach, et. al. [10] have surveyed a number of TM^{2+}:MX materials systems with the express interest in their use as room temperature, diode-pumped mid-IR tunable lasers.

THE Cr^{2+}:ZnX (X = S, Se, Te) LASER MATERIAL SYSTEM

Figure 3 shows the energy levels of several divalent transition metal ions substituted for Zn in ZnSe (T_d site symmetry), taken from Fazzio [11]. Several factors identify the Cr^{2+} ion as a likely effective laser ion emitting in the mid-IR. First the lowest-lying excited state (^5E) is separated from the ground $^5T_2$ level for about 4800 cm^{-1} (providing pump and luminescence bands in the desired spectral region. The Tanabe-Sugano energy level diagram of the $Cr^{2+}(d^4)$ ion in T_d coordination is shown in Figure 4. The DqB values for the ZnSe and ZnS crystal lattices are indicated. According to Figure 4, we would expect to Cr^{2+} ions in these lattices to exhibit strong (spin-allowed) pump absorption bands near 1700 nm, and strong Stokes-shifted emission bands centered at ~2400 nm. Figure 5 shows the ^5E - $^5T_2$ absorption and emission bands for ZnS, ZnSe, and ZnTe crystals doped with Cr^{2+} ions [10], along with measured temperature-dependent luminescent lifetimes. The absorption and emission bands are just as expected. The luminescence

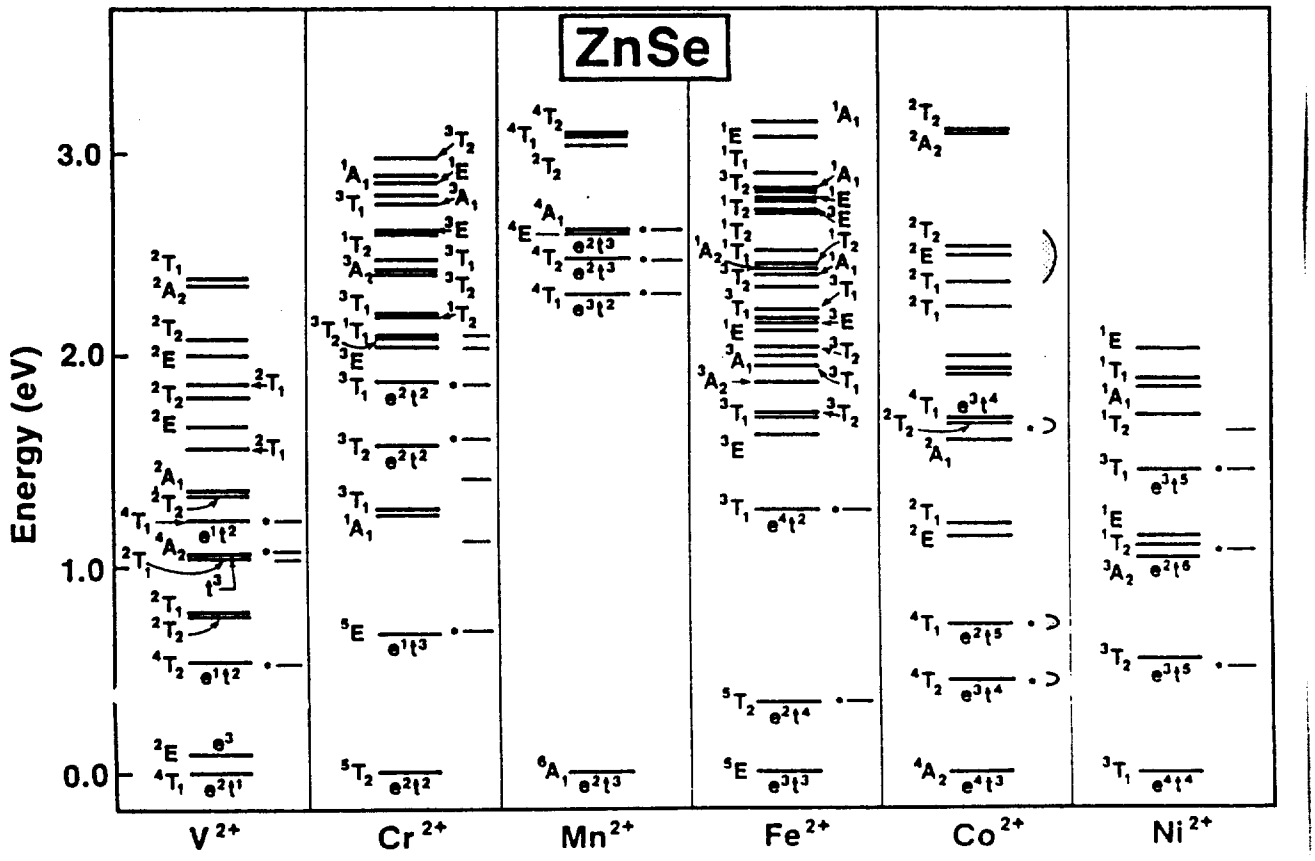

Figure 3. Electronic energy levels of divalent transition metal ions in ZnSe (after Fazzio [11].

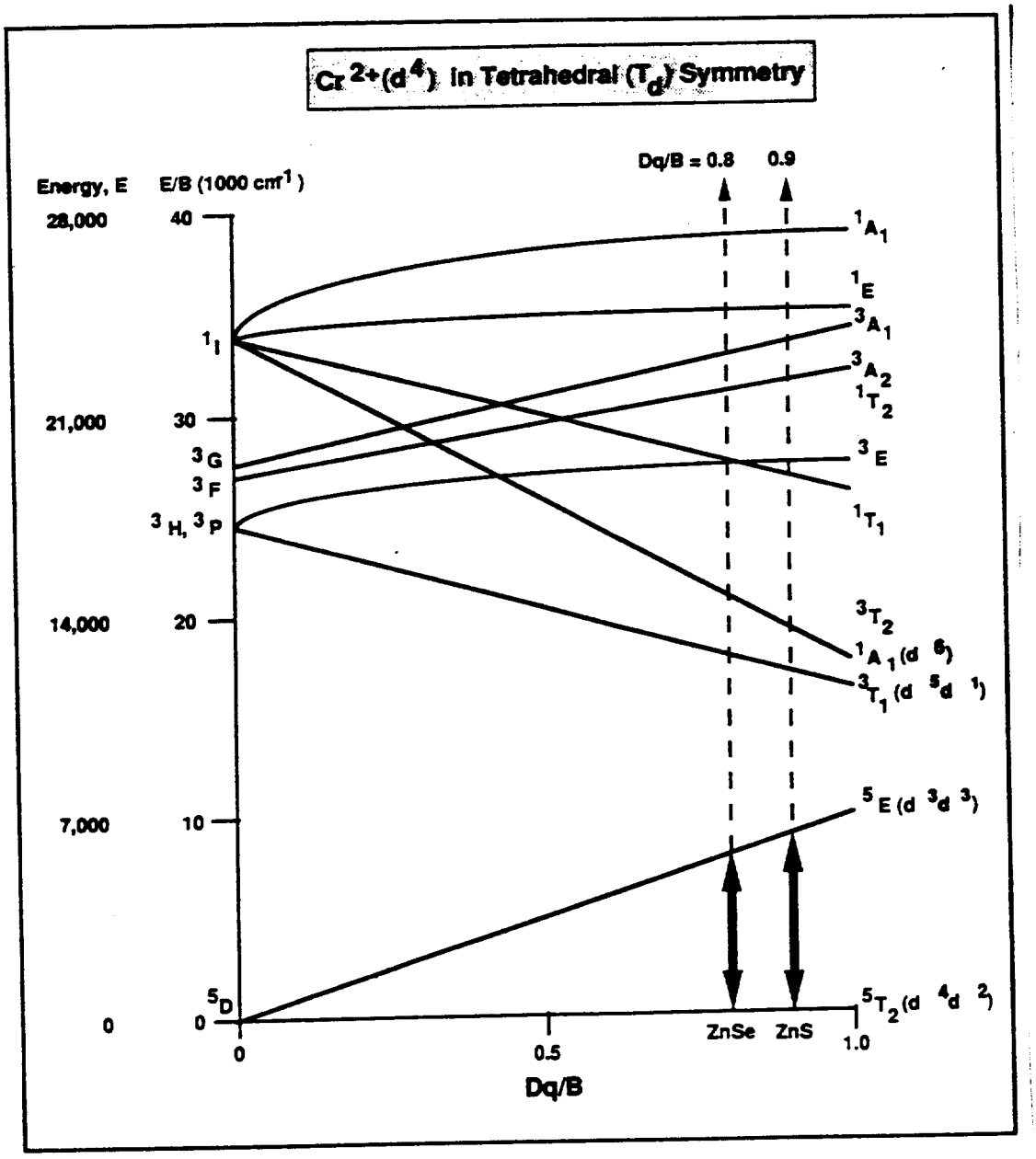

Figure 4. Tanabe-Sugano energy level diagram for Cr^{2+} ions in T_d coordination. DqB values for ZnSe and ZnS crystal lattices are indicated. The $^5T_2$ - ^5E transition near 2400 nm is identified as a candidate laser transition.

lifetimes are characteristically a few microseconds long, increasing slowly with temperature from low temperature to near room temperature, and then decreasing above room temperature. These data are in general agreement with previously reported data in the literature [12-15]. The observed characteristic temperature dependence can be reasonably interpreted as being consistent with essentially radiative decay for temperatures up to room temperature. The rather short radiative decay times (microseconds) corresponds to the rather large calculated (stimulated) emission cross sections indicated in Figure 5. In order to attain efficient laser action, it is also important that the gain medium be essentially free of excited state absorption at pump and laser wavelengths. In of the case of the Cr^{2+} ion in T_d coordination, all of the electronic levels lying above the upper laser (^5E) level are either singlets or triplets, and one can anticipate at most only weak excited state absorption at the pump and/or laser wavelengths.

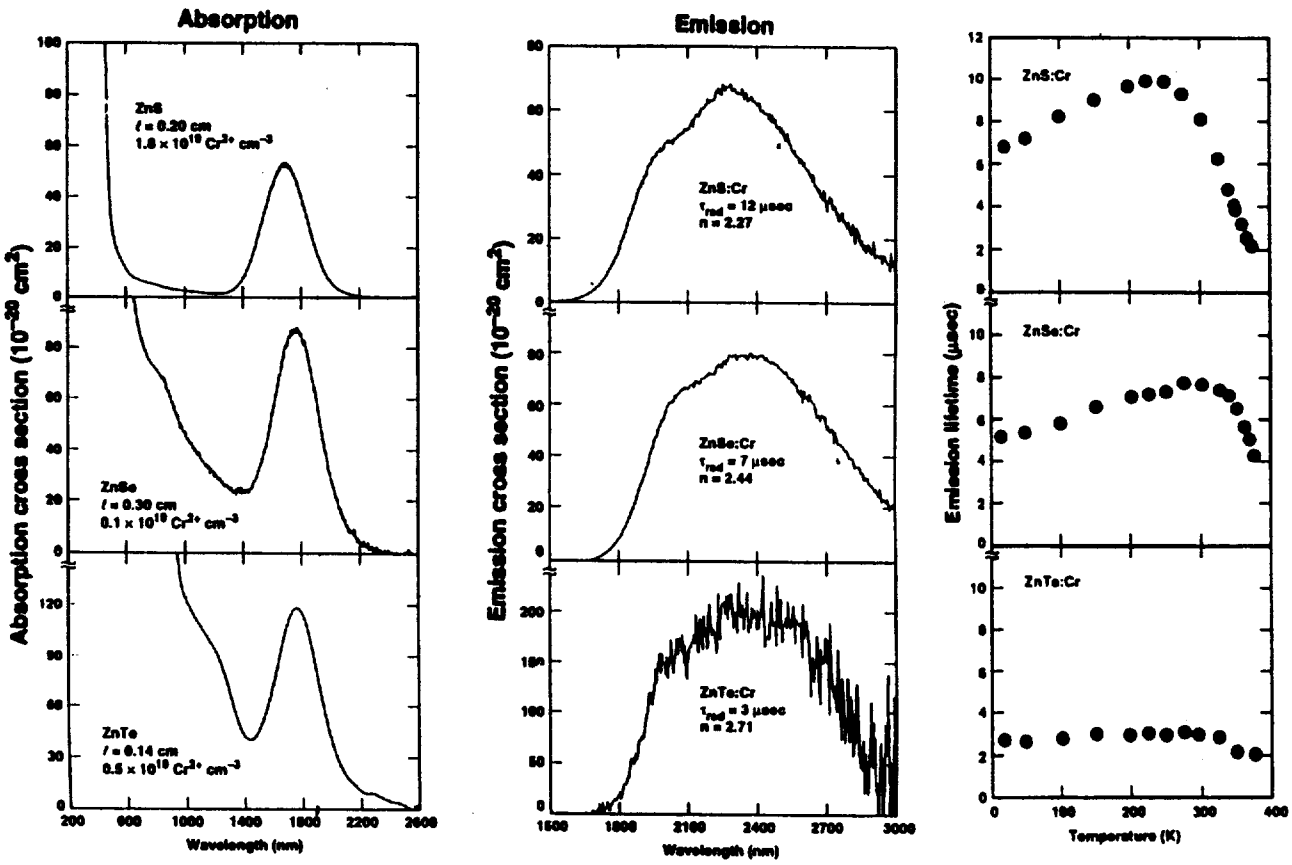

Figure 5. Room temperature absorption and emission spectral of ZnSe, ZnS, and ZnTe doped with Cr^{2+} ions. Temperature dependence of the decay times of the $^5T_2$ - ^5E luminescence centered near 2400 nm.

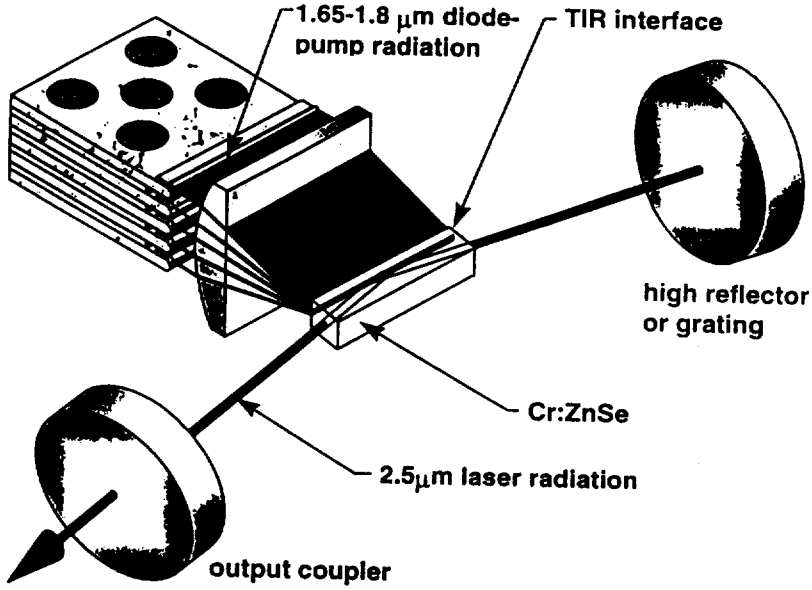

Figure 6. Diode-side-pumped Cr^{2+}:ZnSe laser design. A five-bar stack of GaInAsP laser diode pump array transversely pumps the gain crystal. The laser cavity resonator contains a single reflection from the face of the gain element nearest the diode pump array [18].

Cr^{2+}:ZnSe LASER EXPERIMENTS

Successful demonstrations of laser action have been carried out by DeLoach, et. al. [10] and by Page, et. al. [16,17,18]. To perform these laser experiments, laser gain crystals of ZnSe doped with Cr^{2+} ions were prepared in several ways, including doped Bridgeman [10], vapor phase transport [16,17], and diffusion doped CVD [17]. These experiments have been analyzed and reported in the literature [10, 16, 17]. A maximum slope efficiency of 30% was observed. When free running without an intra-cavity tuning element present, the laser oscillated at a wavelength of ~2350 nm, quite near the peak of the luminescence curve. Using a birefringent filter as a tuning element in the cavity, a tuning range from 2280 to 2530 nm was observed. In subsequent experiments using a grating tuning element, Page [18] observed a much broader tuning range (665 nm) from 2134 to 2799 nm, essentially over the entire luminescence (gain) band. These results indicate, as expected, that there is little if any excited state absorption near the luminescence band. This result is consistent with the photoconductivity measurements reported for Cr^{2+}:ZnSe [19].

More recently, Page [18] has demonstrated a diode-pumped Cr^{2+}:ZnSe laser. A four bar stack of high power GaInAsP diodes emitting near 1650 nm was designed and fabricated as the pump source for this laser. The pump array bars were fitted with collimating microlenses to ensure a high transport and focusing efficiency in the laser gain medium. The Figure 6 shows a schematic of the diode pumped laser layout. The array output was brought to a line focus (0.2 mm high) on one of the slab laser crystal faces. The laser crystal was relatively lightly doped, providing a pump absorption coefficient of only 4.4 cm^{-1}. The ends of the slab are anti-reflection coated at 2500 nm. A single bounce at the pumped crystal surface allows the resonated cavity mode to experience high laser gain, yet enter and exit the crystal without significant aperture losses. Figure 7 shows a plot of the observed laser output energy as a function of the absorbed pump energy. Analysis of the output/input data with different coupling fractions indicates that the passive crystal loss at the laser wavelength is ~15%/cm. Efforts are now under way to reduce the loss coefficient while increasing the amount of Cr^{2+} in the crystal. These preliminary laser results suggest that efficient and effective diode pumping of the Cr^{2+}:ZnSe are quite feasible, and that compact high performance Cr^{2+}:ZnSe tunable lasers can be expected with a wide variety of output waveforms possible.

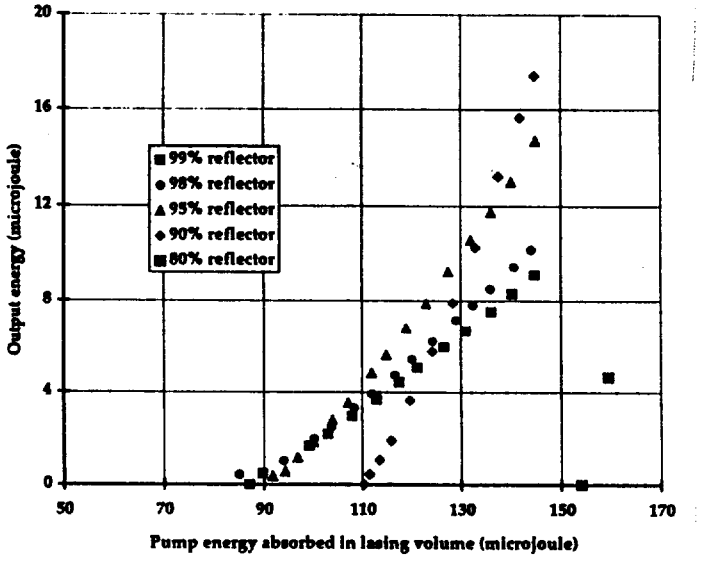

Figure 7. Slope efficiency data for the diode-pumped Cr^{2+}:ZnSe laser for several different flat output coupler mirrors. The pump energy axis has been scaled to account for an estimated mode fill factor of 0.06.

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